PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

| Applicant's or agent's file reference | FOR FURTHER ACTION | see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below. |
|---|---|---|
| AA 1335 PCT | | |
| International application No. | International filing date *(day/month/year)* | (Earliest) Priority Date *(day/month/year)* |
| PCT/GB 98/00705 | 09/03/1998 | 10/03/1997 |
| Applicant | | |
| JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al. | | |

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. [ ] **Certain claims were found unsearchable** (see Box I).

2. [ ] **Unity of invention is lacking** (see Box II).

3. [ ] The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
   - [ ] filed with the international application.
   - [ ] furnished by the applicant separately from the international application,
     - [ ] but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
   - [ ] Transcribed by this Authority

4. With regard to the **title,**
   - [ ] the text is approved as submitted by the applicant
   - [X] the text has been established by this Authority to read as follows:

   EMISSION CONTROL SYSTEM FOR A LEAN-BURN INTERNAL COMBUSTION ENGINE

5. With regard to the **abstract,**
   - [X] the text is approved as submitted by the applicant
   - [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this International Search Report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is:

   Figure No. _____
   - [ ] as suggested by the applicant.
   - [ ] because the applicant failed to suggest a figure.
   - [ ] because this figure better characterizes the invention.

   [X] None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 98/00705

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 661 089 A (RIKEN KK) 5 July 1995<br>see page 2, line 39 - page 3, line 49<br>see page 4, line 12 - line 13<br>see page 5, line 1 - line 9<br>see page 5, line 45 - line 46; claims 1-10; examples 27-38; tables 20-27<br>see page 6, line 7 - line 16 | 1-10 |
| A | DE 26 49 825 A (FORD WERKE AG) 26 May 1977<br>see page 5 - page 11; figures 4,5 | 1,3,5,6, 8,10 |
| A | EP 0 514 591 A (CORNING INC) 25 November 1992<br>see page 2, line 55 - page 3, line 38<br>see page 4, line 33 - line 55<br>see page 6, line 2 - line 39; examples 1-5 | 1-10 |

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 June 1998 | 25/06/1998 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Cubas Alcaraz, J |

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 93 04767 A (FORD MOTOR CANADA ;FORD WERKE AG (DE); FORD FRANCE (FR); FORD MOTO) 18 March 1993<br>see page 3, line 9 - line 36; figures 1-3<br>see page 8, line 1 - line 14 | 1,4-6,9, 10 |
| A | EP 0 707 883 A (N E CHEMCAT CORP) 24 April 1996<br>see the whole document | 1 |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/00705

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| EP 0661089 A | 05-07-1995 | JP 2587000 B | 05-03-1997 |
| | | JP 7232036 A | 05-09-1995 |
| | | DE 69408957 D | 16-04-1998 |
| | | JP 8024583 A | 30-01-1996 |
| | | JP 7265701 A | 17-10-1995 |
| | | JP 8024646 A | 30-01-1996 |
| DE 2649825 A | 26-05-1977 | CA 1073363 A | 11-03-1980 |
| | | GB 1548243 A | 11-07-1979 |
| | | JP 52065177 A | 30-05-1977 |
| EP 0514591 A | 25-11-1992 | US 5168085 A | 01-12-1992 |
| | | AT 125725 T | 15-08-1995 |
| | | AU 648362 B | 21-04-1994 |
| | | AU 8898991 A | 26-11-1992 |
| | | DE 69111796 D | 07-09-1995 |
| | | DE 69111796 T | 18-04-1996 |
| | | JP 5096133 A | 20-04-1993 |
| | | MX 9200151 A | 01-01-1993 |
| WO 9304767 A | 18-03-1993 | CA 2115040 A | 18-03-1993 |
| | | DE 69208377 D | 28-03-1996 |
| | | DE 69208377 T | 20-06-1996 |
| | | EP 0641245 A | 08-03-1995 |
| | | JP 6509983 T | 10-11-1994 |
| | | MX 9204701 A | 01-03-1993 |
| EP 0707883 A | 24-04-1996 | JP 8103656 A | 23-04-1996 |
| | | CA 2159956 A | 07-04-1996 |

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

# PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

United States Patent and Trademark Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

| | |
|---|---|
| **Date of mailing** (day/month/year)<br>19 October 1998 (19.10.98) | |
| **International application No.**<br>PCT/GB98/00705 | **Applicant's or agent's file reference**<br>AA 1335 PCT |
| **International filing date** (day/month/year)<br>09 March 1998 (09.03.98) | **Priority date** (day/month/year)<br>10 March 1997 (10.03.97) |
| **Applicant**<br>TWIGG, Martyn, Vincent | |

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

28 September 1998 (28.09.98)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

| | |
|---|---|
| **The International Bureau of WIPO**<br>**34, chemin des Colombettes**<br>**1211 Geneva 20, Switzerland** | Authorized officer<br>A. Karkachi |
| Facsimile No.: (41-22) 740.14.35 | Telephone No.: (41-22) 338.83.38 |

## CLAIMS

1. An emission control system for a lean-burn internal combustion engine, comprising (A) a first catalyst system, comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000$hr^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, and (B) a second catalyst system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

2. A control system according to claim 1, wherein the first catalyst system is such that the exhaust gases from the engine flow over it at a space velocity below 40000$hr^{-1}$.

3. A control system according to claim 1 or 2, wherein the second catalyst system is such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000$hr^{-1}$.

4. A control system according to any one of the preceding claims, wherein the first catalyst system and the second catalyst system each contains platinum.

5. A control system according to any one of the preceding claims, wherein the first catalyst system is ahead of the second catalyst system in the exhaust apparatus of the engine.

6. A process for the control of emissions from a lean-burn internal combustion engine, comprising passing exhaust gases from the engine over a first catalyst system, comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000$hr^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, then passing the product gases exiting from the first catalyst system over a second catalyst

REPLACED BY ART 34

system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

7. A process according to claim 6, wherein the gases are passed over the first catalyst system at a space velocity below 40000$hr^{-1}$.

8. A process according to claim 6 or 7, wherein the gases are passed over the second catalyst system at a space velocity of 40000-80000$hr^{-1}$.

9. A process according to any one of claims 6-8, wherein the first catalyst and the second catalyst system each contains platinum.

10. A process according to any one of claims 6-9, wherein the engine is in a vehicle.

# PATENT COOPERATION TREATY

# PCT

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| Applicant's or agent's file reference | FOR FURTHER ACTION | See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416) |
|---|---|---|
| AA 1335 PCT | | |
| International application No. | International filing date *(day/month/year)* | Priority date *(day/month/year)* |
| PCT/GB98/00705 | 09/03/1998 | 10/03/1997 |
| International Patent Classification (IPC) or national classification and IPC<br>B01D53/94 | | |
| Applicant<br>JOHNSON MATTHEY PUBLIC LIMITED COMPANY et al. | | |

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 8 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 2 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☒ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

| Date of submission of the demand | Date of completion of this report |
|---|---|
| 28/09/1998 | 01.07.99 |
| Name and mailing address of the international preliminary examining authority:<br>European Patent Office<br>D-80298 Munich<br>Tel. (+49-89) 2399-0 Tx: 523656 epmu d<br>Fax: (+49-89) 2399-4465 | Authorized officer<br>Czech, B<br>Telephone No. (+49-89) 2399 8627 |

Form PCT/IPEA/409 (cover sheet) (January 1994)

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB98/00705

## I. Basis of th report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-7 as originally filed

**Claims, No.:**

1-8 as received on 27/02/1999 with letter of 24/02/1999

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☒ the claims, Nos.: 9,10
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have b en considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

## III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

☐ the entire international application.

☒ claims Nos. 1-8 (no final opinion).

because:

☐ the said international application, or the said claims Nos. relate to the following subject matter which does not require an international preliminary examination (*specify*):

☒ the description, claims or drawings (*indicate particular elements below*) or said claims Nos. 2,3 are so unclear that no meaningful opinion could be formed (*specify*):

**see separate sheet**

☒ the claims, or said claims Nos. 1-8 are so inadequately supported by the description that no meaningful opinion could be formed.

☐ no international search report has been established for the said claims Nos. .

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|---|---|---|---|
| Novelty (N) | Yes: | Claims | --- |
| | No: | Claims | --- |
| Inventive step (IS) | Yes: | Claims | --- |
| | No: | Claims | --- |
| Industrial applicability (IA) | Yes: | Claims | --- |
| | No: | Claims | --- |

2. Citations and explanations

**see separate sheet**

## VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

**see separate sheet**

## VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separat sheet**

## A. Re Item VIII *(Certain observations on the international application)*

A.1 Since the engine is not part of the arrangement covered by present (apparatus) claim 1, present claims 2 and 3 do not make any sense, since the gas flow (method features) depends inter alia on the type of engine (exhaust gas output) used. An intended method of using the catalyst system does not imply any limitations as to the constructional and/or compositional features of the catalyst system itself.

A.2 The engine not being part of the arrangement of claim 1, the features "upstream" and "downstream" incorporated into present claim 1 do not in any way impose restrictions on the catalytic system as such, in terms of the order in which the gases are contacted with the catalysts.

A.3 The intended method of use "suitable for lean burn engine" is not considered to imply any limitations on the catalytic system as such, in terms of the construction and/or composition of the catalysts. On can only conclude from this statement that the properties referred to in claim 1 are to be measured under lean conditions.

A.4 Claim 1 does not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claim attempts to define some of the features of the device according to claim 1, ie the types of catalysts used, in terms of their desirable oxidation/reduction properties. This is equivalent to a mere statement of the technical problem to be solved, without any indication of how such properties may be obtained.
The application comprises examples which show how such properties can be obtained, ie by using low "loadings" and low space velocities in the upstream catalyst (see also p.7, last paragraph). However these measures (constructional features) are in no way reflected in the independant claims.
It is thus questionable whether the claims are fully supported (Art.6 PCT) as far as catalysts with similar properties obtained some other way are concerned, and/or whether the skilled person would be aware of alternative ways of obtaining such catalyst properties (sufficiency of disclosure, Art.5 PCT)

A.5 The admissibility of the disclaimer ("no silver or tungsten") is objectionable. There is no basis in the text of the present application as originally filed for excluding tungsten (a base metal), whereas the exclusion of silver (neither a Pt group metal nor a base metal) appears to be acceptable on the basis of the text (p.2, 3rd paragraph) as far as the first catalyst is concerned, but not as far as the 2nd catalyst is concerned (see p.3, l.10 "other components").
For establishing novelty over D1 (the sole purpose of a disclaimer), the exclusion of Ag from the first stage catalyst would appear to be sufficient.

A.6 Some passages of the description refer to the invention in a different way than the claims. See in particular page 1, paragraphs 3 and 4 and page 7, line 25 ("combination according to the invention"), to be contrasted with the wording of present independant claims 1 and 5.
These inconsistencies do also lead to certain doubts concerning the scope of the claims (Art.6 PCT).

A.7 The description has not been adapted to the amendments carried out in the claims.

**B. Re Item III** *(Non-establishment of opinion with regard to novelty, inventive step and industrial applicability)*

B.1 Due to the above objections, a final assessment of novelty and inventive step (Art.33(1)(2)(3) PCT) cannot be made.

B.2 No meaningful opinion was possible for claims 2 and 3 in view of the objections raised under item A.2.

**C. Re Item V** *(Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement)*

C.1 **D2 = EP-A-0 514 591** discloses a two stage catalyst. The first, upstream catalyst comprises Rh and optionally Pt and/or Pd and is used for reducing the **major part**

of the NOx to $N_2$. The second downstream catalyst comprises a noble metal, eg Pt and/or Pd and performs the oxidation of remaining HC and CO. The catalyst may be used with "lean" exhaust gases, with optional addition of reducing agents (as in the present application, see p.4, 2nd paragraph). D2 mentions "low loadings" in the sense of the present application. See in particular D2, claims 1 and 10-12, p.4, l.2-7 and l.35-44, p.6, l.26-39.

C.2 The conditions used in D2 in the measuring of the catalyst properties differ in terms of temperature (600°C), space velocity (50000/hr) and gas composition. The only differences, if any, of the presently claimed subject-matter over the prior art disclosed in D2 thus consist in the properties of the first and second catalysts used, which are expressed in parameter form, the parameters being measured by a non-standard method.

C.3 The burden of identifying differences in terms of properties, composition or structure between the present invention and the prior art is with the applicant. However, the applicant has not submitted any evidence or arguments showing that the two stage catalysts disclosed in D2 do not fall under the scope of present claims 1 and 4.

C.4 Therefore, at the present stage, the subject-matter of claims 1 and 4 is considered to lack novelty over D2 (Art.33(1)(2) PCT). Consequently, claims 5, 7 and 8 lack novelty or at least inventive step as well (Art.33(1)(2) PCT).

C.5 **D4 = EP-A-0 707 883** discloses a two-step catalyst system for purifying lean ($O_2$ excess) exhaust gases. Both zones comprise at least one of Pt,Pd,Rh,Ir. In a first zone, the catalyst acts primarily as HC oxidation catalyst. The catalyst in the downstream zone performs NOx reduction to $N_2$ in an essentially HC free environment. See in particular D4, claims 1,2,4. This document is thus irrelevant as far a the claimed process is concerned. Since the relative arrangement of the two catalysts and the engine is not specified in present claims 1-4 (see items A.1 and A.2 above), D4 is however highly relevant for the subject-matter of these claims 1 and 4.

C.6 In particular, examples 2 and 3 of D4 disclose systems comprising two different Pt-catalysts in series, ie catalysts (1)+(4) and (2)+(4), respectively. From figures 1 and 2 it can be seen that catalysts (1)and (2) achieve very high conversions of HC and CO at 230°C and a space velocity of 30000/hr (see col.13, l.24, this value is used in all examples). It can thus be assumed that at 25000/hr, the values to be reached by the second catalyst referred to in present claim 1 would also be obtained. On the other hand, under the same measuring conditions catalyst (4) leads to a ratio of NOx conversion to HC conversion of more than 0.2 (see figures 6 and 7 of D4), even though the HC:$NO_x$ ratio is only 1.5 : 1. It can thus be assumed that at 25000/hr and at HC:$NO_x$ ratios of 3:1, the values to be reached by the first catalyst referred to in present claim 1 would also be obtained.

C.7 The applicant has not submitted any evidence or arguments showing that the two stage catalysts disclosed in D4 do not fall under the scope of present claims 1 and 4. Therefore, at the present stage, the subject-matter of claims 1 and 4 is considered to lack novelty over D4 (Art.33(1)(2) PCT).

C.8 **D1 = EP-A-0 661 089** (see the passages mentioned in the search report) discloses systems for the purification of lean exhaust gases from internal combustion engines comprising two catalysts arranged in series in the exhaust gas flow path. According to one embodiment, both catalysts comprise Pt-group metals. The purpose of the first catalyst is to reduce the NOx present to $N_2$. The purpose of the second catalyst is to oxidise the remaining HC and CO. Space velocities of 30000$h^{-1}$ are mentioned (see eg examples 27 and 31-33).
However, it is clearly emanates from D1 that silver is the essential component of the first stage catalyst, whereas the presence of silver (not a base metal, not a platinum metal) is not addressed in the present application (see p.2, 2nd paragraph).
With a proper delimitation over D1 (see item A.5 above), this document would therefore have to be disregarded in assessing novelty and inventive step.

C.9 **D3 = DE-A-26 49 825** discloses a two stage catalyst. The first catalyst comprises Rh or Ir is used for selectively reducing the NOx to $N_2$. The second downstream catalyst comprises Pt and/or Pd and performs the oxidation of remaining HC and CO. See in particular D3, claims 1-6 and pages 3-4, page 6, 3rd paragraph. The

catalyst is said to be suitable for being operated with slightly "lean" exhaust gases (see p.10, l.4-8 and figure 5). However, A/F ratios of 14.7 are not mentioned, there might be a mistake in the values indicated: The stoichiometric point ("Redoxpotential = 1") is indicated at A/F = 14.48. This is in contradiction with what is said in D5, p.1, l.16-22 (same company as D3) and in D2, p.4, l.40-41. Moreover, in addition to these ambiguities, the data concerning the catalysts used as indicated on p.9, last paragraph, are not detailed enough to suggest or disclose the properties of the catalysts as defined in present claim 1.

C10 **D5 = WO-A-93 04767** discloses a two-stage catalyst system for purifying lean exhaust gases (A/F>14.7). However, the first stage is different in that it comprises a transition metall loaded onto a refractory oxide and a zeolite as active elements.

C11 The industrial applicability of the subject-matter disclosed clearly emanates from the description (Art.33(1)(4) PCT).

## D. Remarks

D.1 The presence of novel and inventive subject-matter is not excluded. Possibly, a combination of engine and catalyst system designed to give space velocities < 40000/hr in the first stage, and "low loadings" of the first stage catalyst, as well as a corresponding process comprising these features, could be considered to fulfill the requirements of Art.33 PCT.

## E. Re Item VII *(Certain defects in the international application)*

E.1 Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D1-D4 is not mentioned in the description, nor are these documents identified therein.

1553

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 53/94 — A1

(11) International Publication Number: WO 98/40153

(43) International Publication Date: 17 September 1998 (17.09.98)

(21) International Application Number: PCT/GB98/00705

(22) International Filing Date: 9 March 1998 (09.03.98)

(30) Priority Data:
9705010.8 10 March 1997 (10.03.97) GB

(71) Applicant (*for all designated States except US*): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2–4 Cockspur Street, London SW1Y 5BQ (GB).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): TWIGG, Martyn, Vincent [GB/GB]; 108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB).

(74) Agent: BREWER, Leonard, Stuart; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).

(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
*With international search report.*

(54) Title: EMISSION CONTROL SYSTEM FOR A LEAN–BURN INTERNAL COMBUSTION ENGINE

(57) Abstract

An emission control system for a lean–burn internal combustion engine comprises (A) a first catalyst system comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230 °C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, and (B) a second catalyst system, which has, as measured under the same conditions, à % hydrocarbon conversion of greater than 80 % and a % carbon monoxide conversion of greater than 70 %.

09/380864
514 Rec'd PCT/PTO 09 SEP 1999
WO 98/40153 PCT/GB98/00705

# EMISSION CONTROL SYSTEM FOR A LEAN-BURN INTERNAL COMBUSTION ENGINE

This invention concerns improvements in emissions control systems, and more especially it concerns improvements in emissions control for engines operating at lean air/fuel ratios, *ie* air/fuel ratios greater than 14.7, generally in the range 19-50.

It will be appreciated that with lean-burn engines of various types, including particularly diesel, lean-burn gasoline and direct injection gasoline engines, the control of NOx tends to be difficult. This is understandable in that the exhaust gases contain relatively high amounts of oxygen and hence the removal of NOx involves reduction of NOx to $N_2$ in an overall oxidising atmosphere. Prior proposals have involved storage of NOx in the emission control system until a time when the exhaust gas contains relatively less oxygen, that is until the engine is running "rich", *eg* during acceleration. Another proposal is to store unburnt hydrocarbon until a point at which it can be released to contribute to NOx reduction. There remains the need, however, for yet further systems and strategies to achieve control of NOx emissions under lean conditions.

The present invention provides a novel emission control system for a lean-burn internal combustion engine, comprising a first catalyst system comprising platinum group metal and having relatively high selectivity for NOx reduction, and a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide. By platinum group metal is meant platinum and/or palladium and/or rhodium.

The invention also provides a process for the control of emissions from a lean-burn internal combustion engine, comprising passing the exhaust from the engine over a first catalyst system comprising platinum group metal and having relatively high selectivity for NOx reduction, and then passing the product gases exiting from said first catalyst system over a second catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide.

By selectivity for NOx reduction is meant the ratio of %NOx conversion to % hydrocarbon conversion. The catalyst system having relatively high such selectivity has a

selectivity of at least 0.2, preferably at least 0.3, especially at least 0.4; this is as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane. The catalyst system having high activity for the oxidation of hydrocarbons and carbon monoxide has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80%, preferably greater than 90%; it has, as measured under the same conditions, a % carbon monoxide conversion of greater than 70%, preferably greater than 80%, especially greater than 90%, particularly greater than 95%. Defining the catalyst systems according to measurement under these conditions does not mean of course that they are necessarily operated under these conditions. In a particular embodiment, the first catalyst system is such that the exhaust gases from the engine flow over it at a low space velocity, particularly below 40000hr$^{-1}$. The second catalyst system is usually such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000hr$^{-1}$. The first catalyst system usually contains platinum. The second catalyst system usually contains platinum. Thus, in a particular embodiment each contains platinum. For use, the first catalyst system can be mounted ahead of the second catalyst system in the exhaust apparatus of the engine. The present engine is preferably in a vehicle, for example a passenger car or heavy duty truck.

The skilled person may apply the present invention in a variety of ways. The first catalyst system may be, for example, a relatively low loading of catalytically active component on a substrate, optionally in combination with components that can retain NOx and/or reducing species, such as zeolite or like absorbents, or alkaline earth metal compounds. We have discovered that reducing the loading of catalytically active component (comprising platinum group metal, particularly platinum, optionally in the presence of base metal components) compared to conventional exhaust gas catalysts, serves to increase the selectivity of the catalyst system towards NOx reduction. The first catalyst system can contain for instance platinum group metal, particularly platinum, in amount less than 30g/ft$^3$ (30g per 0.028m$^3$).

In a particular embodiment, the first catalyst system provides a low space velocity. Normal space velocities for exhaust catalysts systems are 40000-80000hr$^{-1}$. A lower space

velocity may be achieved readily in practice by increasing the volume of the catalyst, or by utilising two catalyst "bricks" in parallel.

The second catalyst system is required to be of high oxidation activity. Such catalyst need not have NOx selectivity, but must be capable of oxidising hydrocarbons and carbon monoxide under the reaction conditions, to the desired extent, usually so as to satisfy emission standards regulations. Normal space velocities may be used. The second catalyst system usually comprises platinum group metal, particularly platinum, optionally in the presence of base metal components. A suitable oxidation catalyst comprises platinum on a high surface area support, optionally with other components which promote such oxidations.

The skilled person is very familiar with conventional exhaust gas catalyst technology. Generally, a support which is a honeycomb-type extruded ceramic or wound metal monolith or "brick" is coated with a surface area-enlarging washcoat, for example a washcoat consisting of or comprising alumina. Deposited onto the washcoat is a coating of one or more catalytic components, optionally with one or more other components such as ceria, zirconia, zeolite or the like, and the catalyst may be multi-component deposited in discrete layers or some components may be layered, with other components distributed throughout such layers. In the present invention, the actual catalysts chosen, and their construction, are not critical providing they meet the criteria stated.

It is now well established that carbon monoxide and hydrocarbons play a part in the reduction of NOx. For example, taking the hydrocarbon as $C_3H_6$, the following reactions could take place:

$$18NO + 2C_3H_6 - 9N_2 + 6CO_2 + 6H_2O$$

$$2NO + 2CO - N_2 + 2CO_2$$

The molar ratios required for NOx reduction, namely $C_3H_6$ to NO and CO to NO, are exceeded over the European test cycle on average with a diesel engine. However, there

is competition between NOx and oxygen for the reducing species, and normally only quite low NOx conversions, (*eg* much less than 10%) are achieved in the European test cycle.

It may be preferred to increase NOx conversion under certain conditions by increasing the relative quantity of hydrocarbons in the exhaust. For example, injection of fuel into the exhaust upstream of the first catalyst system may be used. Alternatively, hydrocarbon storage using zeolites or the like, may be useful. It will be appreciated that there would be a small fuel consumption penalty if fuel injection into the exhaust is used. The high activity second catalyst system is readily capable of catalysing the oxidation of any excess hydrocarbons under the lean conditions.

Conventional catalyst manufacturing technology may be used.

The first and second catalyst systems may be mounted in a single "can" in the exhaust system, or they may be separated by a length of exhaust pipe.

The present engine is generally a diesel, lean-burn gasoline or direct injection gasoline engine.

The present invention is illustrated by the following Tests.

Test 1

The increase of NOx selectivity corresponding to decreasing platinum loading was shown for a standard 6in (15.2cm) catalyst brick. Exhaust from a 1.9 litre turbo direct injection diesel bench engine, operating at steady state conditions was used. NOx selectivity is measured as % NOx conversion at 230°C/% hydrocarbon conversion at 230°C. The results are shown in Table 1 below.

TABLE 1

| Pt loading (g/ft$^3$) (g/0.028m$^3$) | NOx selectivity at 230°C |
|---|---|
| 10 | 1.00 |
| 25 | 0.40 |
| 50 | 0.34 |
| 75 | 0.33 |
| 100 | 0.31 |

A reduced loading of catalyst therefore improves selectivity.

Test 2

The increase in NOx conversion, at a constant platinum loading (1.5g) *per* catalyst brick, by decreasing space velocity and reducing loading in g/unit volume was measured. The same engine and conditions was used as in Test 1. The NOx conversion was measured with "raw" exhaust from the engine ("Passive") and with the addition of hydrocarbon (HC) into the exhaust to yield a HC3:NOx ratio of 2.0:1. HC3 means that the hydrocarbon is counted as equivalent propane.

TABLE 2

| Catalyst length inches (cm) | Maximum NOx Conversion (%) | |
|---|---|---|
| | Passive | Added HC |
| 1 (2.5) | 6 | 13 |
| 2 (5.1) | 12 | 17 |
| 3 (7.6) | 16 | 22 |
| 4 (10.1) | 18 | 25 |
| 5 (12.7) | 22 | 29 |
| 6 (15.2) | 25 | 33 |

It can clearly be seen that increasing catalyst length and hence decreasing space velocity is beneficial in overall NOx conversion.

## EXAMPLE 1

A 1996 model passenger car with a 2.5 litre turbo direct injection diesel engine was used with several different exhaust catalyst systems, for standard EUDC emission tests (Extra Urban Driving Cycle emission tests of the European Union). The results are shown in Table 3 below.

TABLE 3

**Catalyst System**

| | HC | CO | NOx | HC+ NOx | PM (4) | %NOx |
|---|---|---|---|---|---|---|
| No Catalyst | 0.322 | 1.034 | 0.394 | 0.715 | 0.089 | 0.0 |
| OEM Catalyst (1) | 0.196 | 0.913 | 0.389 | 0.585 | 0.081 | 1.3 |
| New Catalyst (2) | 0.067 | 0.336 | 0.332 | 0.399 | 0.079 | 15.7 |
| Lean-NOx Catalyst (3) | 0.054 | 0.495 | 0.294 | 0.347 | 0.073 | 25.4 |
| Lean-NOx Catalyst + Oxidation Catalyst (5) | 0.037 | 0.237 | 0.292 | 0.329 | 0.077 | 25.9 |

Notes:

(1) OEM (Original Equipment Manufacturer) catalyst, 6in (15.2cm) long, with 46g/ft$^{-3}$ (g per 0.028m$^3$) Pt.

(2) Advanced oxidation catalyst, 6 in (15.2cm) long with 40g/ft$^{-3}$ (g per 0.028m$^3$) Pt.

(3) Lean-NOx catalyst, 12 in (30.5cm) long, with 25g/ft$^{-3}$ (g per 0.028m$^3$) Pt.

(4) PM = Particulate Matter, g/km

(5) Lean-NOx catalyst, 9in (22.9cm) long, with 25g/ft$^{-3}$ (g per 0.028m$^3$) Pt. followed by oxidation catalyst, 3in (7.6cm) long, with 100g/ft$^{-3}$ (g per 0.028m$^3$) Pt.

All the catalysts used were fresh, *ie* without ageing.

It can readily be seen that the low loading, low space velocity Lean-NOx Catalyst is very effective in converting NOx, and that the combination according to the invention is remarkably effective.

## CLAIMS

1. An emission control system for a lean-burn internal combustion engine, comprising (A) a first catalyst system, comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, and (B) a second catalyst system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

2. A control system according to claim 1, wherein the first catalyst system is such that the exhaust gases from the engine flow over it at a space velocity below 40000hr$^{-1}$.

3. A control system according to claim 1 or 2, wherein the second catalyst system is such that the exhaust gases from the engine flow over it at a space velocity of 40000-80000hr$^{-1}$.

4. A control system according to any one of the preceding claims, wherein the first catalyst system and the second catalyst system each contains platinum.

5. A control system according to any one of the preceding claims, wherein the first catalyst system is ahead of the second catalyst system in the exhaust apparatus of the engine.

6. A process for the control of emissions from a lean-burn internal combustion engine, comprising passing exhaust gases from the engine over a first catalyst system, comprising platinum group metal selected from platinum and/or palladium and/or rhodium, which catalyst system has a ratio of % NOx conversion to % hydrocarbon conversion of at least 0.2 as measured at a temperature of 230°C, a space velocity of 25000hr$^{-1}$ and a hydrocarbon:NOx input ratio of 3:1 counting the hydrocarbon as equivalent propane, then passing the product gases exiting from the first catalyst system over a second catalyst

system, which has, as measured under the same conditions, a % hydrocarbon conversion of greater than 80% and a % carbon monoxide conversion of greater than 70%.

7. A process according to claim 6, wherein the gases are passed over the first catalyst system at a space velocity below 40000$hr^{-1}$.

8. A process according to claim 6 or 7, wherein the gases are passed over the second catalyst system at a space velocity of 40000-80000$hr^{-1}$.

9. A process according to any one of claims 6-8, wherein the first catalyst and the second catalyst system each contains platinum.

10. A process according to any one of claims 6-9, wherein the engine is in a vehicle.

# INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/GB 98/00705

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C. [X] Patent family members are listed in annex.

* Special categories of cited documents :

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"E" earlier document but published on or after the international filing date
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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 June 1998 | 25/06/1998 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Cubas Alcaraz, J |

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# INTERNATIONAL SEARCH REPORT

Int. ional Application No
PCT/GB 98/00705

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